

DECLARATION OF Alix Gicquel UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS

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SIR:

I, Alix Gicquel, being duly warned, hereby declare and state:

1. I received two Ph.D. one in chemical engineering (University Paris 6, 1981) the other in physical sciences (University Paris 6, 1987) and I am currently employed as a Professor in Chemical Engineering since 1990 (University Paris 13), and as director of USAR- CNRS (support unit of the Agence Nationale de la Recherche), in France. I have been conducting research and development in the field of chemical engineering and physical sciences for twenty years. I am the author/co-author of more than 120 reviewed papers and I have participated in more than 160 conferences.

2. I am also the inventor/co-inventor of 2 patents/patent applications.

3. My scholarly interests include the modeling, design, diagnostics, and control of plasma-assisted materials processes and processing machines. This work focuses on plasma dynamics understanding in order to (1) determine the dominant processes for a given objective, and (2) to enhance the right local parameters to improve a system. The work is based on the one hand on diagnostic studies including a variety of techniques including optical emission spectroscopy, laser spectroscopy diagnostics, and on the other hand, it is based on development of models, including electromagnetism, plasma dynamics, and plasma chemical models, for the design and control of microwave plasma reactors used for materials processing. Specific processes I studied include high quality single crystal, poly-crystal and nano-crystal diamond CVD deposition, nitride thin film formation, atom recombination during atmosphere re-entry shuttles and general radio-frequency and microwave-generated plasma discharges operated as ion and radical sources.

4. I have carefully reviewed the following references:

- US Patent, number 5,626,922 "Miyanaga",
- US Patent application N° 2006/0153994 "Gicquel"

5. I note that Miyanaga and Gicquel concern the technical field of pulsed plasma in films deposition. Miyagana patent concerns more specifically diamond-like-carbon films, while Gicquel patent concerns diamond deposition.

6. Gicquel aims for increasing the microwave power density of the discharge during the pulse (on plasma state) at a constant mean power, and so for improving crystalline diamond film deposition rate and quality without an overheating of the deposition chamber (reducing the temperature of walls on which hydrogen atoms contained in the plasma at high power densities recombine easily). Consequently the low-power states and high-power states duration are chosen to maintain a high dissociation of the hydrogen while limiting the mean microwave power needed.

7. The pressure ranges discussed by Gicquel are from 100 mbar to 350 mbar (whereas Miyanaga pressure ranges are from 0.039 mbar to 39 mbar). It has to be noted that a higher microwave power density (in W/cm^3) in continuous regime strongly increases the wall temperature. The primary dissociation mechanism of the molecular hydrogen is thermal dissociation. Accordingly Gicquel is directed to pulsed plasma rate that maintains the general thermal gas temperature of the discharge (while maintaining the microwave power at a lower value than in the non-pulsed case).

8. As for Miyanaga, the goal is to improve the film (mostly diamond-like-carbon) properties including crystal size, film uniformity and adhesion to substrate. More particularly, Miyanaga results to a changing of the electron temperature and density. Indeed Miyanaga discloses the use of magnetic field pressure from 0.03 to 30 Torr (see for example col. 2, line 47), so the plasma key parameters which are electron energy and density can be improved. As a matter of fact, in this pressure ranges the plasma primarily operates through electrons which are provided from the gases introduced such as hydrogen and hydrocarbons. So a driving dynamic in the plasma is the change of the temperature and density of the electrons. The process is based on the use of an electromagnetic field, which is able (at these pressure range) to accelerate the electrons (through electron cyclotron resonance mechanism or hydride mechanism at 30 Torr). With more energy, the primary electrons may ionize more the gases increasing then the electron density (called plasma density).

9. In the pressure regime discussed by the Gicquel patent (100 mbar to 350 mbar—higher than the Miyanaga patent pressure range), the main mechanism is the molecular hydrogen dissociation which is thermally activated (needs gas temperature much higher than 2500 K). Then to the contrary of Miyanaga, Gicquel operates in applying pulsed energy in order to increase the gas temperature and to simultaneously reduce the volume and also the surface atomic hydrogen recombination by reducing the off plasma duration to 2 ms as well as the wall heating while choosing time parameters (of the pulsing) to control the plasma gas temperature, whereas Miyanaga only applies pulsed energy to reduce the energy consumption and improve the (diamond-like-carbon) film properties without emphasising details of applied microwave power density, plasma pressure or temperatures. Gas temperature in the Miyanaga process is around 300 to 400 K, while in the Gicquel process its range in the plasma bulk is 3500 K to

5000K. On the contrary, the temperature of the electrons in the Miyanaga process must be as high as possible, while in the Gicquel process it is less than 2 eV (low temperature for electrons). In the Gicquel process, ECR (electron cyclotron resonance) cannot occur due to the high pressure. In the Miyanaga process, the plasma is in a strong non equilibrium state (4 temperatures characterize the system: electronic, vibrational, rotational and gas temperatures), while in the Gicquel process, the plasma is only defined by two temperatures (electron and gas temperatures), since there is an equality between vibration, rotation and translation (gas) temperatures.

10. As a result, the diamond microstructure and DLC structure, as well as growth rate obtained by Miyanaga are different from the diamond microstructure and growth rate obtained by Gicquel for a given mixture of hydrocarbon/hydrogen mixtures. Indeed, in the conditions of deposition described in Gicquel, the Diamond-Like-Carbon films of Miyanaga would be destroyed. More precisely, DLC can not bear temperatures higher than 500°C (or even less, the limit depending on the microstructure and the composition of the films – amorphous carbon or nanostructured carbon with various amounts of Hydrogen); the process disclosed in Miyanaga could not be used in order to obtain the same results as Gicquel.

11. Miyanaga and Gicquel should be distinguished in that Miyanaga discloses the use of pulse energy in order to grow diamond, but the growth speed is very low (Miyanaga method may apply to other objectives, such as surface control, or multi-thin-layer deposition...), while Gicquel aims at performing the high speed growth of thick monocrystalline diamond.

12. I further declare that all statements made herein of my own knowledge

are true and that all statements made on information and belief are believed to be true;
and further, that these statements were made with the knowledge that wilful false
statements and the like so made are punishable by fine or imprisonment, or both, under
Section 1001 of Title 18 of the United States Code and that such wilful false statements
may jeopardize the validity of this application or any patent resulting therefrom.

A handwritten signature in black ink, appearing to read 'Alix Gicquel', with a stylized, cursive script.

Alix Gicquel
Date : August 10th, 2009.